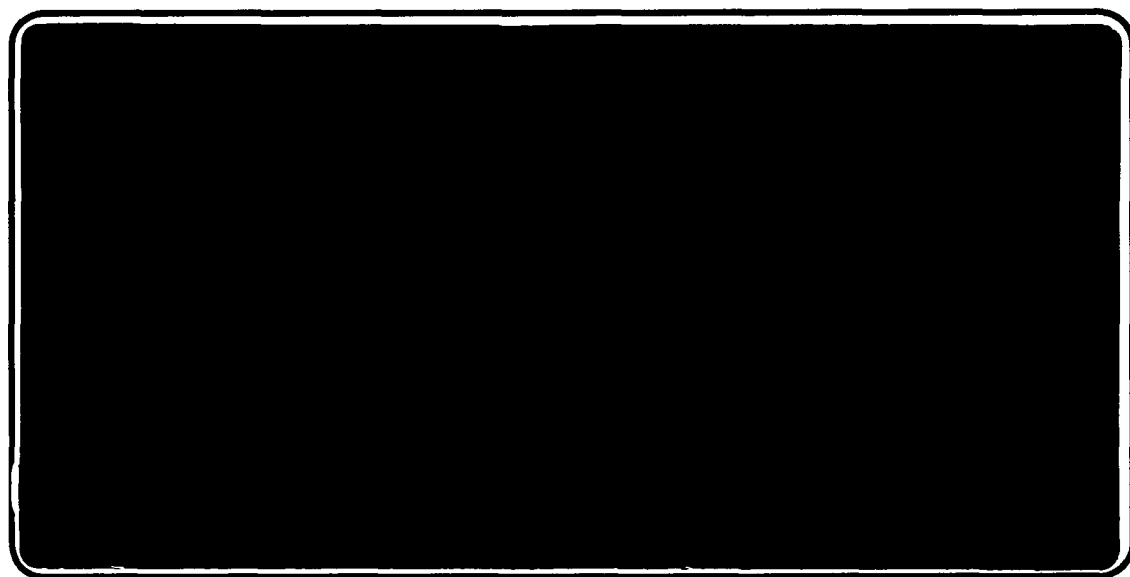




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**CHARACTERIZATION OF FIBER-FIBER BOND STRENGTH
FROM PAPER MECHANICAL PROPERTIES**

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Characterization of Fiber-Fiber Bond Strength
from Paper Mechanical Properties

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CHARACTERIZATION OF FIBER-FIBER BOND STRENGTH FROM PAPER MECHANICAL PROPERTIES

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ABSTRACT

Fiber to fiber bonding is central to sheet strength. This study compares three experimental methods which are purported to correlate with fiber-fiber bond strength. They are z-direction tensile strength, Z-toughness (delamination test), and out-of-plane (ultrasonic) elastic stiffness. A 47.5% yield, unbleached kraft loblolly pine pulp was beaten to several freenesses. These were classified to remove the fines. Handsheets were prepared from the whole and classified pulps at a series of wet pressing pressures and with and without the addition of a polymeric strength aid. Each of the three z-direction tests produced a family of curves as a function of freeness and wet pressing as others have found for in-plane tensile properties. No simple relationship among the three was found. The out-of-plane elastic stiffness was shown to be primarily determined by the density of the sheet and was not a sensitive indicator of the enhanced bonding produced by the strength aid. Increasing amounts of fines produced higher Z-toughness values than did fibrillation of the fibers. Both Z-toughness and z-direction tensile tests provided sensitive measures of the fiber-fiber bonding. The energy consumed during delamination was much greater than that required to create the new interface but was directly proportional to the tensile energy absorption measured in a standard tensile test.

INTRODUCTION

Sheet strength is a function of two factors: individual fiber strength and fiber-fiber bond strength. The latter is a product of the number of bonds, the average area per bond, and the strength of such bonds. Typically, this product is factored into the fraction of the fiber surface that is bonded to another fiber (that is, relative bonded area or RBA) and the shear strength of a bond. Theories have been developed (1-3) to predict the sheet strength from a knowledge of the fiber and bond properties and the geometry of the network. Although satisfactory methods exist for the determination of fiber properties and of RBA, there is no generally agreed upon technique to provide the bond shear strength. Retulainen and Ebeling (4) utilized a number of previously suggested methods on a series of handsheets formed from a

bleached kraft pine pulp. The different methods produced contradictory trends with increasing refining.

Because of increasing use of lower basis weights, higher filler contents, more hardwood, and more secondary fiber, papermakers will need to enhance bond strength chemically in order to maintain and upgrade sheet specifications. To obtain optimum efficiency from these expensive strength aids, we need to improve our fundamental understanding of their roles on both a molecular and fiber network level. The latter requires a sensitive method to evaluate the bond strength. In the work to be described, we examine three methods that directly measure fiber-fiber bonding in paper. The results are compared with calculations using the Page theory (1) and with single fiber-fiber measurements (5).

The z-direction tensile test (6, 7) is the oldest of the three. Although sensitive, its major drawback is time. For well-bonded sheets it is necessary to attach the paper to the mounting cylinders with an epoxy cement (7). This necessitates a lengthy time of cure under compression. Care must be exercised to prevent migration of the adhesive into the bulk of the sheet where it could influence the sheet strength. Anderson (8) has compared double-sided adhesive tape with a more rigid adhesive. He found a consistent but nonlinear relation at higher strengths.

The delamination test is also old (9, 10) but has been recently applied to paper by Skowronski and Bichard (11). It is sensitive and relatively rapid. Further discussion of its potential shortcomings will be deferred to a later section.

The measurement of the several moduli of paper by wave propagation at ultrasonic frequencies has been extensively studied in recent years (12, 13). It has been found that for paper a linear relation holds between the in-plane ultrasonic modulus measured in a given direction and the corresponding tensile strength (14). This correlation is the basis for commercial instrumentation to measure "strength" on-line. It has also been postulated that the out-of-plane moduli (longitudinal and shear) should be related to the degree of bonding in the sheet. Such nondestructive measurements are rapid and precise and have the potential for on-line applications.

The three techniques produce, respectively, a strength, an energy (or work), and a modulus. It is not clear *a priori* whether there should be correlations among them and which should be most sensitive to "bond strength."

MATERIALS AND METHODS

Pulps

Loblolly pine chips were kraft cooked to an unscreened yield of 47.5% and a kappa number of 34.7. The cooked chips were passed through a Sprout-Waldren disc refiner with 10 mil plate separation for defiberization. Portions of this pulp were beaten in a Valley beater to freenesses of 600, 350, or 200 mL CSF. Portions of each beaten pulp were classified on the IPST web former. The fines were saved for later addition in known amounts to the classified pulps. Because it was impractical to save the white water itself, it was allowed to stand overnight and the excess water was decanted from the settled fines. This procedure undoubtedly led to a loss of soluble hemicelluloses and perhaps of colloidal size fines although the decantate was "water clear." The consistency of the saved fines was about 0.3%. The whole and classified pulps were dewatered to about 25-30% solids (depending upon their freeness). Formaldehyde was added to the pulps and to the fines as a preservative, and they were stored at 4 °C until used.

The amount of fines in the beaten whole pulps was determined by screening through a Britt jar with 76 μm holes. For the 600, 350, and 200 mL CSF pulps, the percent fines were 5.3, 7.5, and 11.1, respectively.

Fiber properties were measured on the classified pulps. No effect of refining was found on fiber length or width. The weighted average of the length (third moment of the number distribution function) was 3.1 mm while the arithmetic average width was 33 μm . The fiber perimeter and coarseness were 78 μm and 28 $\mu\text{g}/100\text{m}$, respectively. The zero-span tensile index was independent of the level of refining and strength aid addition (see below) but decreased upon removal of fines from 129 to 108 Nm/g.

Handsheets

Standard Noble & Wood handsheets were formed from the (never-dried) pulps in deionized water adjusted to a pH of 5 with sulfuric acid. The nominal basis weight was 60 g/m². They were couched onto blotters and pressed for 5 minutes at either 0, 138, 345, 690, or 1380 kPa. After pressing they were dried on a steam drum under a tensioned felt at 105 °C.

Some of the sheets were treated with chemical additives to enhance their strength. A dilute solution of polyamide-amine-epichlorohydrin (PAE) was added at a dosage of 1% based on the fiber to the pulp at 0.5% consistency. After mixing for 5 minutes a dilute solution of carboxymethylcellulose (CMC) was added to the slurry at a dosage of 0.4% based on the fiber. A further 5 minutes of mixing assured that the

polymers were completely adsorbed on the pulp before sheet formation (15). This combination of a cationic polymer followed by an anionic polymer has been shown to substantially enhance tensile (16) and compressive (15) strength and fiber-fiber bond strength (5).

The sheets were conditioned at 50% RH and 23 °C before testing. In addition to the standard tensile measurements, we tested the sheets for short-span compressive strength (STFI), soft platen caliper (IPST), and in-plane ultrasonic moduli (longitudinal and shear).

Z-Direction Tensile Strength (ZDT)

Measurements were carried out according to the Tappi standard method (17) for values of ZDT less than 700 kPa. The method of Wink and Van Eperen (7) using an epoxy resin as the adhesive was employed for the stronger sheets.

Z-Toughness (G_z)

The method used is essentially the same as that previously described (11) with the exception that the wheel is provided with an air bearing to eliminate friction. The extension rate was 25.4 mm/min and the sample width was 44.5 mm.

The stress distribution in the region of the delamination ("peeling") as a function of peeling angle has been analyzed by Kaelble (18). In general, the geometry leads to mixed mode failure. That is, there are contributions from both z-direction separation and in-plane shear. The relative amounts of each depend on the corresponding moduli and the thickness of the sample as well as the peel angle. For the 90 ° peel angle and the relatively thin samples (60 g/m²) used here, the shear component should be negligible as should the work of bending in the region of delamination. Delamination forces that were independent of basis weight in the range 40 to 60 g/m² support the assumption of primarily Mode I failure.

A more serious objection to the test is that the measured value (an energy) includes irreversible work of deformation of the surrounding fiber network adjacent to the delamination zone. However, the order of magnitude difference in moduli (and strength) between the out-of-plane and in-plane directions suggests that deformation in the latter will be negligible. It is possible that (partial) delamination may occur in adjacent layers. If the resultant surface separation is below optical resolution (<300 nm), the calculated specific Z-toughness (see below) will be too large. Again, the relative weakness of the sheet in the z-direction would tend to confine the failure to the primary delamination layer where the stresses are maximal.

It has been shown (19, 20) that the delamination force (i.e., force per unit sample width) is equivalent to the work of peeling per unit area or the energy absorbed in deformation and fracture per unit area of new (geometric) surface. Skowronski and Bichard (11) recognize this but choose to call the quantity "bond strength" with units of J/m². To minimize confusion with tensile, compressive, and bond shear strengths (each having units of N/m² or papermakers' units of Nm/g), the measured quantity will be denoted as Z-toughness (G_z) following Schultz-Eklund, Fellers, and Olofsson (21).

By measuring the scattering coefficient of the paper sheet sandwiched between the transparent tapes before and after delamination, the increase in scattering, ΔS , can be determined. The change in optical contact area per unit of geometrical area, ΔOCA , is then

$$\Delta OCA = (\Delta S)(G)$$

where G is the grammage. The bond breaking energy per unit of bond broken optical contact area will be termed the specific Z-toughness (sG_z) and is calculated as

$$sG_z = (G_z) / \Delta OCA$$

This quantity should reflect the inherent "strength" of the bonds in the paper. Note that the optical contact area is much less than the true surface area (although directly proportional to the latter) (22). Thus, sG_z cannot be directly compared with the energy to break particular bonds, e.g., hydrogen bonds.

Out-of-Plane Ultrasonic Moduli

The instrumentation and theory for measurement of the out-of-plane elastic properties has been previously described (23). The results can be expressed in terms of the modulus ($E_z = v^2\rho = C_{33}$, the longitudinal elastic stiffness in the z-direction), where v is the velocity of the longitudinal wave and ρ is the apparent density, which is the ratio of the grammage to the caliper. The out-of-plane shear properties have more error associated with them because of problems of coupling between the transducers and the sample and will not be discussed here.

RESULTS AND DISCUSSION

Determination of RBA

The usual method for calculating RBA begins with the assumption that portions of a fiber not bonded to another fiber scatter light, while the bonded portions (having no interface with air) do not. Haselton (22) put the optical method of determining RBA on a firm basis by showing the linear relationship between the scattering coefficient and the surface area as measured by the BET gas adsorption technique. The RBA can then be defined as

$$\text{RBA} = (S_0 - S) / S_0$$

where S is the scattering coefficient of the sheet, and S_0 is the scattering coefficient of the same fibers in a completely unbonded state. The major difficulty is in obtaining a value for the latter. Ingmanson and Thode (24) suggested extrapolating a plot of S against tensile strength to zero tensile strength for a series of sheets made from the same pulp but with different degrees of wet pressing. The drawback is that such plots are usually nonlinear as we would now expect on the basis of the Page theory (1) and, furthermore, involve long extrapolations. Luner, Karna, and Donofrio (25) showed that plots of S against initial modulus for sheets with different amounts of wet pressing were linear with relatively short extrapolations required to reach zero modulus.

Uesaka (26) has shown that the network theory of Perkins and Mark (27) predicts a linear relation between the sheet modulus and the RBA when $\text{RBA} \ll 1$. From the definition of RBA in terms of the scattering coefficients, this also means that a plot of scattering coefficient against modulus should be linear and extrapolate to S_0 at zero modulus. We have chosen to use the in-plane longitudinal (ultrasonic) stiffness (C_{11}) for the determination because it can be accurately and nondestructively measured. A typical plot is shown in Fig. 1 for the whole pulp treated with the strength aids. The data for four pulps (unrefined and three levels of refining) each at five levels of wet pressing fall on a single curve. Similar plots were made for the other pulps, values for S_0 were determined, and RBA was calculated for the various sheets.

It is of interest to plot the scattering coefficient against the density for the classified pulp. Fig. 2 shows this with both treated and untreated pulp falling on the same curve. If the linear relationship is extrapolated to zero scattering, the corresponding density is 1.62 g/cm^3 , which is close to the value for crystalline cellulose.

Production of Bonding by Densification

Page (28) has reviewed the experimental findings and interpretations of previous workers who have shown that the tensile strength of paper at a given density (or scattering coefficient or RBA) depends on whether that density was achieved via wet pressing or refining. The tensile elastic modulus (29) and the ultrasonically-measured elastic constants (12, 30) have similarly been shown to respond differently to the refining and wet pressing of the fibers. We now show in Figs. 3-5 (classified, untreated pulp) that the z-direction properties behave in a like manner. (Using RBA instead of density as the abscissa does not produce a collapse of the data onto a single curve.) Refining produces a greater enhancement at a given density than does wet pressing. The magnitude of the effect is similar for the ZDT and Z-toughness and much less for C_{33} . Because the slopes of the linear regression fit within, the individual plots are approximately constant, we will use the percent increase of the particular property at a refining level of 200 mL CSF above that at 600 mL CSF at a density of 0.5 g/cm^3 to compare the four different pulps. The results are shown in Table 1.

Table 1. Effect of refining on z-direction properties.

<u>Percent increase due to refining^a</u>			
<u>Pulp</u>	<u>G_z</u>	<u>ZDT</u>	<u>C₃₃</u>
CU ^b	40	70	20
WU	85	75	20
CT	15	nd ^c	0
WT	60	nd	15

^a From 600 to 200 mL CSF

^b C = classified; W = whole; U, T = untreated, treated with strength aids

^c nd = not determined

For Z-toughness removal of fines or addition of a strength aid lowers the effect of refining. Fines appear to have no effect on ZDT. Refining has only a small (but generally finite) effect on the z-direction longitudinal stiffness in agreement with previous work (12).

For the whole pulp the results for the Z-toughness form two distinct envelopes for the untreated and treated samples, respectively, as shown in Fig. 6. Page and co-workers (28, 29) have discussed possible reasons for the differing influences of wet pressing and beating on tensile strength and modulus (and presumably upon other mechanical properties). It is unlikely that curlation or latency effects could be

responsible for the changes we find with beating for this pulp. The other possibility they suggest concerns the presence of crimps, kinks, and microcompressions in the fibers. The more highly beaten a pulp is, the more it will swell in water and the more it will shrink upon subsequent drying. If the drying is carried out under restraint, the shrinkage forces will reduce the fiber defects between bonding sites which results in a tightening of the sheet structure. This effect leads to an increase in the modulus, and the better stress distribution leads to a higher strength. Unfortunately, there is no independent measure of the magnitude of this effect which would allow us to reduce measurements made at different freenesses to a single curve.

Intercomparison of Various Measures of Bonding

The results for the different methods of measuring z-direction properties are compared for the classified, untreated pulp in Figs. 7-9. Similar results were found for the whole and treated pulps. Z-toughness forms a family of curves (as a function of freeness) when plotted against either C_{33} (Fig. 7) or ZDT (Fig. 8). The intercepts at zero C_{33} or zero ZDT are finite and positive.

When ZDT is plotted against C_{33} in Fig. 9, a family of curves at constant freenesses is again found, but the intercept is now close to zero. Linear regression lines are shown. Similar results are also shown for the whole, untreated pulp in Fig. 9. The variation in slope with refining and with fines shows that the two measurements, ZDT and C_{33} , depend differently on these parameters. Previous workers (31) who had performed similar measurements on oriented, wet-strained sheets also found a linear relationship between the two with a finite positive intercept. For the present samples, both whole and classified, linear regression lines can be fit through the origin with only slightly lower correlation coefficients.

Effect of Fines

For the results to be discussed in this section, one factor is different from the results presented elsewhere in this work. Here, where the pulps are treated with a strength aid, PAE alone is used. Although this results in lower values of the strength (15), we chose to use the single component to minimize the complexity of the system. The sequence of additions was:

1. classified pulp
2. fines and water to give a desired percentage of fines based on total solids and a consistency of 0.5%
3. PAE to give a 1% dosage based on the total solids

All other procedures remained the same, except that only one wet pressing level (345 kPa) was employed. The white water from the sheet making was filtered, and the fines lost was determined gravimetrically. From this the percent fines retention and the actual percent fines in the sheet were calculated. These results are presented in Table 2. The cationic PAE acts as a fair retention aid.

Table 2. Fines Retention

<u>Pulp</u>	<u>% Fines Added</u>	<u>% Retention</u>	<u>% Fines in Sheet</u>
Unbeaten	7.5	33	2.6
"	15.0	50	8.1
"	22.5	57	14.2
600C	7.5	60	4.6
"	15.0	63	10.0
"	22.5	65	15.9
350C	7.5	64	4.9
"	15.0	68	10.7
"	22.5	69	16.7
200C	7.5	69	5.3
"	15.0	71	11.1
"	22.5	70	16.9
<u>1% PAE added after fines</u>			
350C	7.5	71	5.4
"	15.0	77	12.0
"	22.5	74	17.7

In the following discussion, we will be comparing treated and untreated pulps. It is important to evaluate the effect of the treatment on the density of the sheets to determine whether the properties can be compared at common densities. Fines were added to the classified pulp (C350) (obtained by removing the fines from the whole pulp that had been beaten to 350 mL CSF). The sheet densities are shown plotted against percent fines in the sheet in Fig. 10. The effect of the PAE treatment on density is negligible. The linear regression line (combining both treated and untreated data) is shown and extrapolates to a value of 1.59 g/cm³ at 100% fines. This density is close to that for crystalline cellulose.

The Z-toughness for pulp 350C is shown plotted against percent fines in the sheet in Fig. 11. There is a linear relationship for both the untreated and treated cases. The

pressing and refining. Apparently, C_{33} is not sensitive at low densities to the additional bond strength provided by the additives but is primarily governed by the density of the sheet.

Seth (32) has argued from the Page theory (1) that the bond strength of a sheet is proportional to the product of b , the bond shear strength, and the RBA. He then postulates that this product should be proportional to the density. For bonding in the absence of additives this is a reasonable statement. However, the results of Figs. 2 and 10 suggest that density is not a good predictor of sheet bond strength when polymeric strength additives are used. The strong dependence of C_{33} on density leads to its insensitivity to the enhanced bond strength produced by additives.

Z-direction tensile strength (ZDT).

Plots of ZDT against density exhibited a family of curves at different refining levels (Fig. 4) and against C_{33} (Fig. 9) (small) nonzero intercepts. A plot of ZDT against RBA for the whole untreated pulps (Fig. 17) again shows a family of curves. Linear regression lines fit through the origin are drawn. The slopes of these which are equivalent to the extrapolated value of ZDT at an RBA of unity are presented in Table 3 along with similar results for the classified pulps.

Table 3. Extrapolated values of ZDT at RBA = 1.

<u>Freeness, mL CSF</u>	<u>Z-direction tensile strength, kPa</u>	
	<u>Classified pulp</u>	<u>Whole pulp</u>
685	----	930
600	690	1080
350	960	1460
200	1310	----

The results for the classified pulps suggest that, in addition to increasing the RBA, refining increases the bond strength. Perhaps this implies improved bonding at the molecular level beyond the changes observed by the light scattering measurement. The results with fines (whole pulp) are about 50% higher, again indicating the importance of fines in bonding.

Z-toughness.

As discussed previously, Skowronski and Bichard (11) have suggested the use of the specific Z-toughness ("specific bond strength") as a measure of the sheet bond strength. A plot of Z-toughness against the change in the optical contact area per unit of geometric area for the treated and untreated classified pulp is shown in Fig. 18. The curves do not extrapolate through the origin, but we may take the slopes as indicative of the energy absorbed per unit optical contact area produced during

delamination. The values for the untreated and treated pulps are 160 and 510 J/m², respectively. The value for the untreated pulp is in good agreement with those found by Skowronski and Bichard (11) which ranged from about 120 to 220 J/m².

Are these reasonable values for the amount of energy needed to break the hydrogen bonds holding the untreated fibers together? First, we must recognize that the optical contact area is much less than the true surface area. Haselton (22) showed that the two are directly proportional. The proportionality constants found by him and by Swanson and Steber (33) ranged from 0.04-0.05 for four different pulps. Taking a mean value of 0.045, we may take the product of it and the specific Z-toughness found above (160 J/m²) to calculate a value of about 7 J/m² for the energy per unit surface area consumed during delamination.

Using an energy for a hydrogen bond of 5 kcal/mole and an area per bond of 0.25 nm² (0.5 nm × 0.5 nm), Nissan (34) has calculated that a reasonable energy to break the hydrogen bonds during delamination would be about 0.13 J/m², which is less than 2% of the value we observe.

What is the source of this discrepancy, which is clearly beyond experimental error? The nonzero intercepts in Fig. 18 imply that energy is being absorbed even when no new surface is being generated. However, this is outside the calculation above, which used the slope rather than the absolute value. Nissan (34) suggests a tortuosity factor: the delamination may meander among adjacent planes within the sheet so that the true new surface area produced will be greater than that measured by the optical technique. A similar alternative would allow partial delamination in layers adjacent to the fracture surface. Either of these explanations might produce additional surface beyond the resolution of the light scattering technique.

Yet another explanation for such large energies was given by Van den Akker (35) to explain similar overly large energies found when determining the Nordman bond strength. He termed it a "force limited" energy. Essentially, strain energy is built up in the network until failure releases it along with the energy of the bond breaking. Finally, it must be recognized that paper is a viscoelastic material, and energy is consumed by irreversible deformation prior to failure and will contribute to that measured during delamination. Use of a strength aid will increase the energy consumed via any of the explanations because they all ultimately rely upon the bonding between the fibers. Hence, the Z-toughness and the specific Z-toughness provide information about the strength of the bonding indirectly. Clearly, more work is needed to better characterize the energy loss mechanisms and their relationship to bonding.

It is of interest to compare the energy absorbed during delamination with that absorbed during the usual tensile stress-strain measurement (tensile energy absorption, TEA). The latter in units of J/g can be multiplied by the density to give

an energy per unit volume. A plot of Z-toughness against TEA is shown in Fig. 19. Data for classified and whole pulps, both treated and untreated, are given. The close correlation suggests that similar mechanisms are at work to consume the energies. The upturn in the bonding energy for strong bonds is an indication that the tensile measurement is at that point being limited by the tensile strength of the fibers as predicted by the Page theory (1).

Finally, we may use the Page equation (1) to calculate a value for the bond shear strength.

$$1/T - 9/8Z = 12C/PLb(RBA)$$

Here, T is the tensile index, Z is the zero span tensile index, C is the fiber coarseness, P is the fiber perimeter, and b is the bond shear strength. The equation can be rearranged so that we may plot $T/(1 - 9T/8Z)$ against RBA. The curve should pass through the origin with slope $PLb/12C$. The data for the treated and untreated classified pulps are so plotted in Fig. 20. Linear regression lines through the origin produced the values for b listed in Table 4.

Table 4. Fiber-Fiber Bond Shear Strength.

<u>Pulp</u>	<u>Treatment</u>	<u>b, MPa^a</u>	<u>b, MPa^b</u>
Class.	Untrtd.	3.1	3.5, 3.7
Class.	Trtd.	10.4	7.5
Whole	Untrtd.	3.7	---
Whole	Trtd.	6.3	---

^a Page equation

^b single fiber studies (5)

Also shown are the values for the whole pulps in this study and values from an experimental study (5) of single fiber-fiber bonds. The agreement among the various samples is good. The ratio between the treated and untreated values is 2-3 which is the same factor found in the measurements of Z-toughness (at a given density) and calculated for specific Z-toughness. Hieta and co-workers (36) have recently determined a bond strength index which may be viewed as a z-direction fiber bond strength. The maximum value they find for their pulps is about 1 MPa. The difference between this value and those presented in Table 4 may reflect the different types of pulp or the different geometries of the tests.

CONCLUSIONS

All three z-direction tests provide good measures of the improvement in bonding created by refining and wet pressing. Unlike the other two, the out-of-plane elastic stiffness was not as sensitive to the enhanced bonding supplied by the chemical strength aid. Fines contribute much more to bonding than does fibrillation of the fiber. The increase in bonding indicated by the specific Z-toughness when a strength aid is used is similar to that calculated from the Page theory and found experimentally in single fiber studies.

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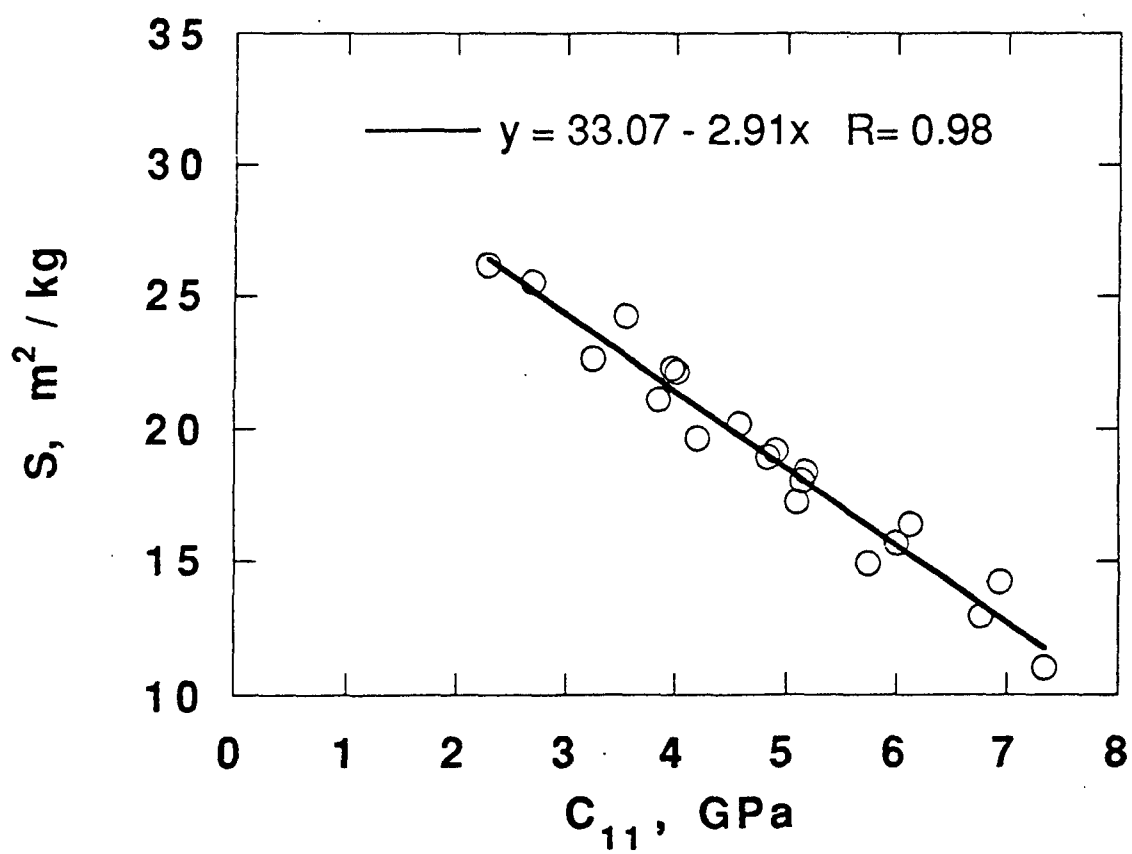


Fig. 1. Scattering coefficient against in-plane stiffness for the whole, treated pulp.

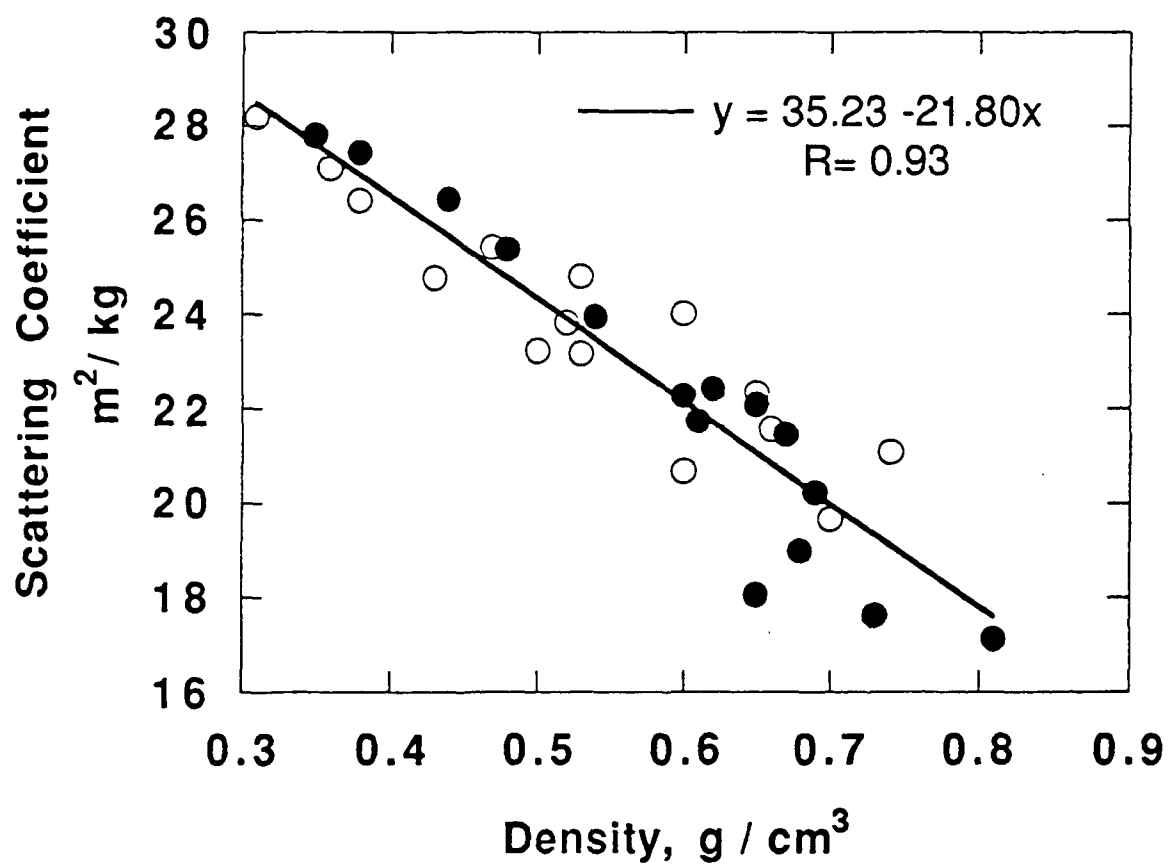


Fig. 2. Scattering coefficient against density for the classified, untreated (open circles) and treated (closed circles) pulps.

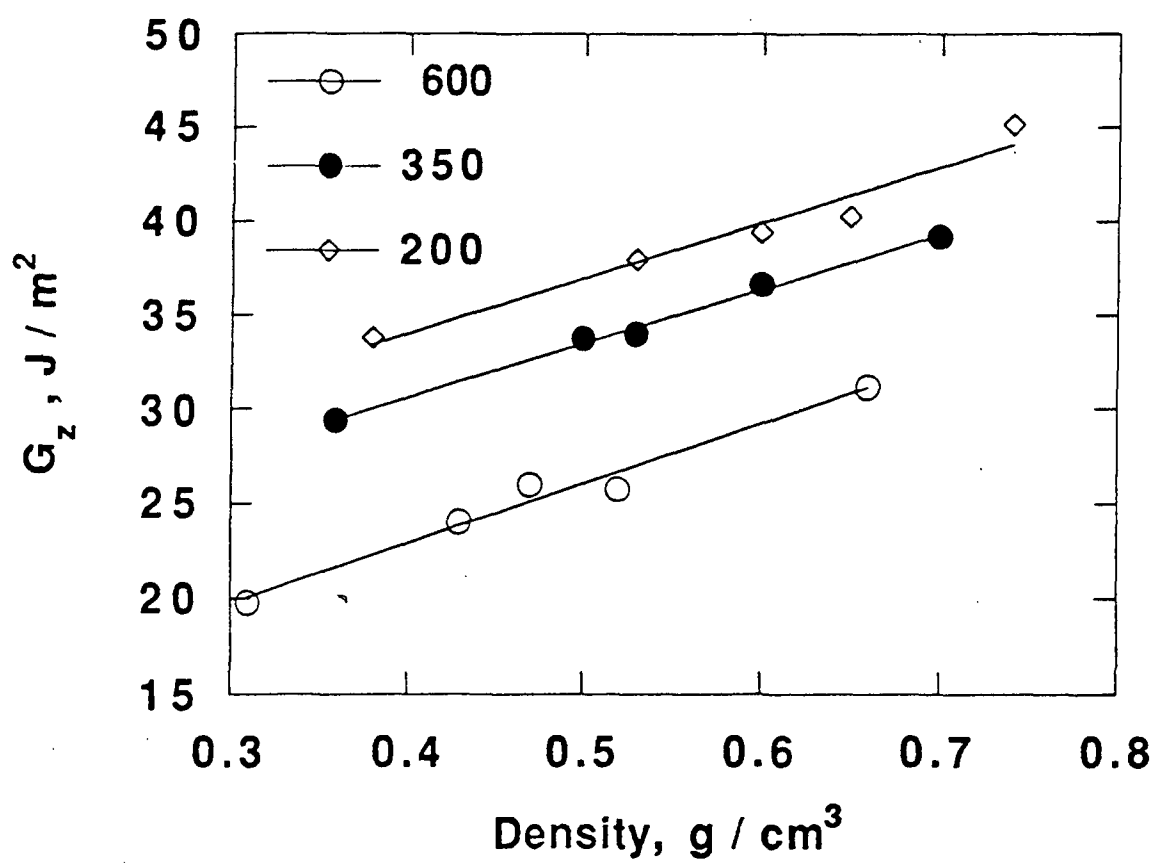


Fig. 3. Z-toughness against density for the classified, untreated pulps at the indicated Canadian standard freenesses.

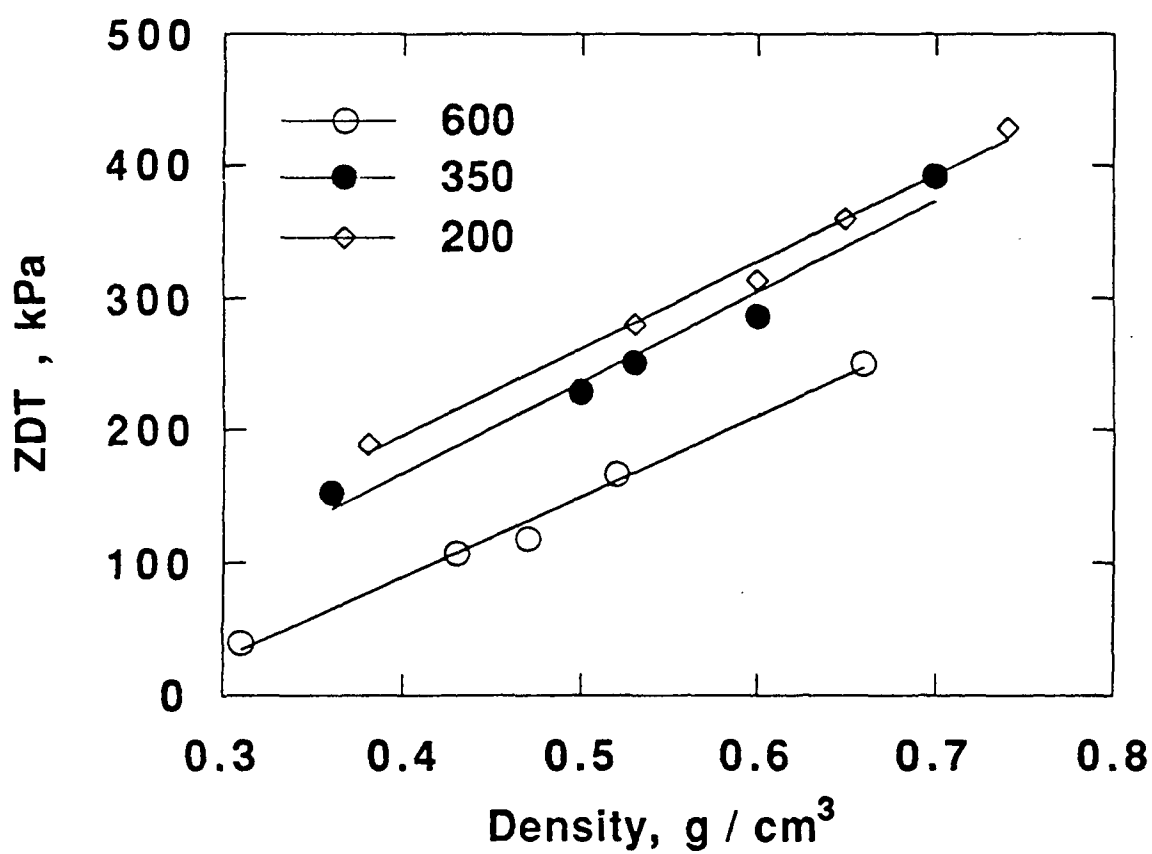


Fig. 4. Z-direction tensile strength as a function of density for the classified, untreated pulps at various freeness levels.

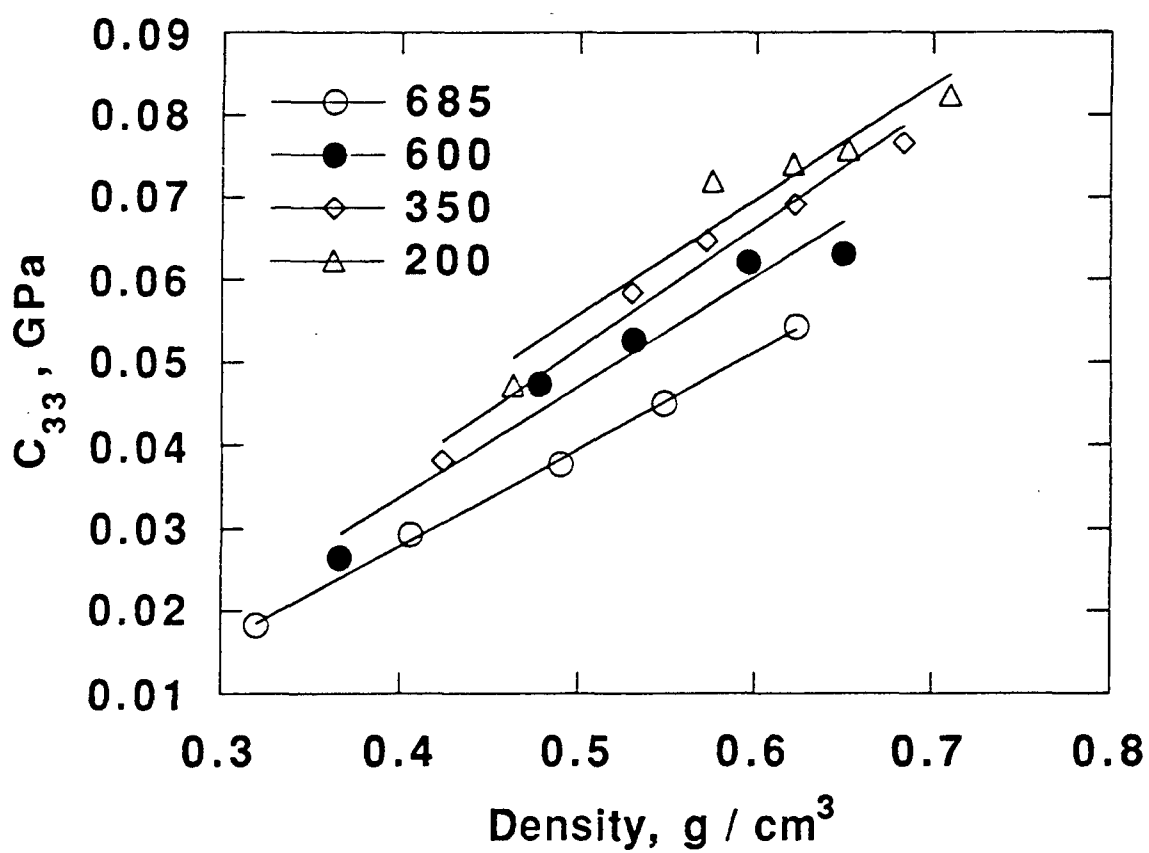


Fig. 5. Out-of-plane longitudinal elastic stiffness as a function of density for the classified, untreated pulps at the indicated freeness levels.

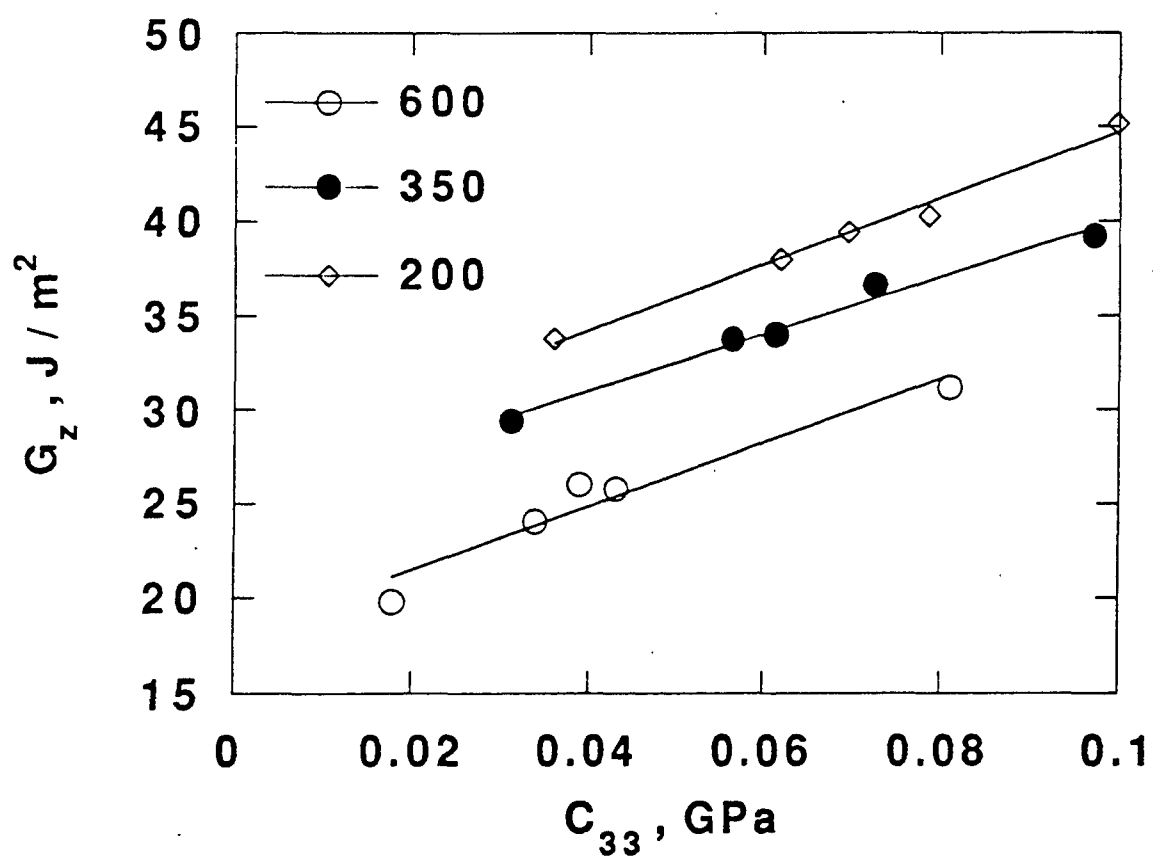


Fig. 7. Comparison of Z-toughness with out-of-plane elastic stiffness for the classified, untreated pulps at different values of freeness.

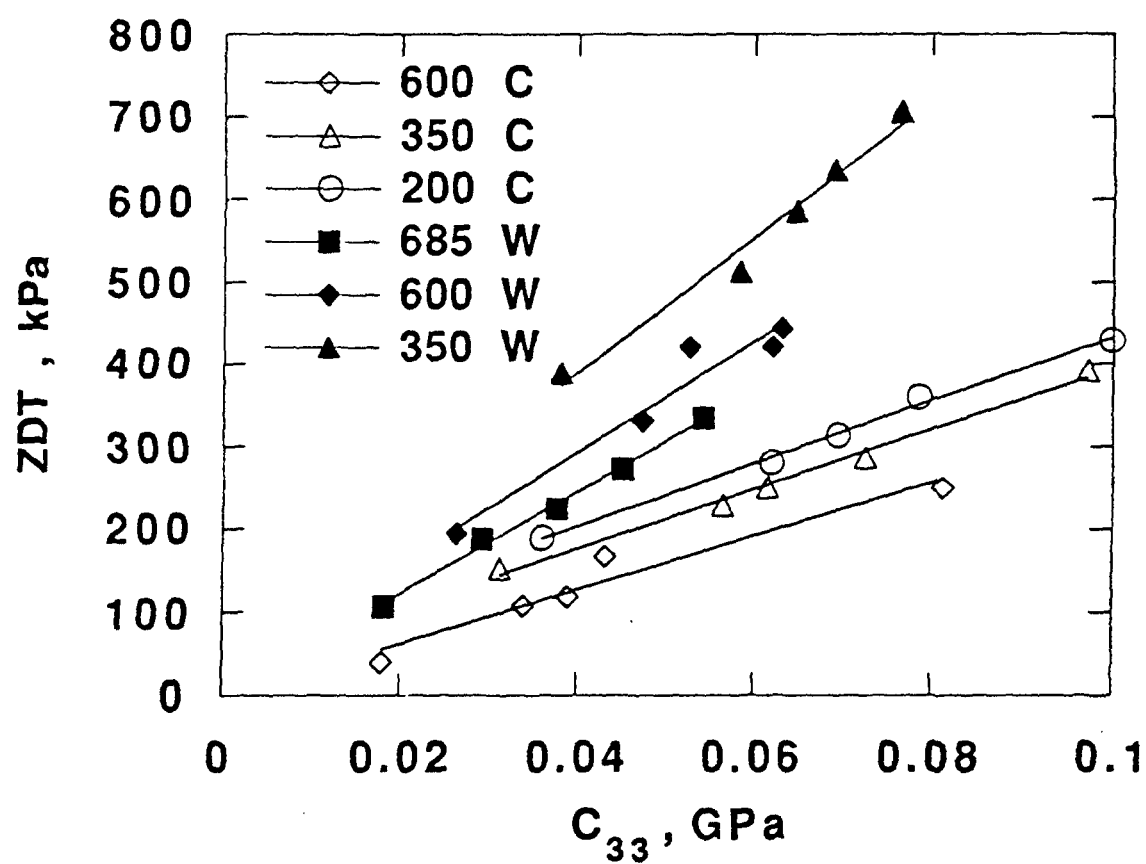


Fig. 9. Comparison of z-direction tensile strength with out-of-plane elastic stiffness for untreated, whole (W) and classified (C) pulps at the indicated freeness levels.

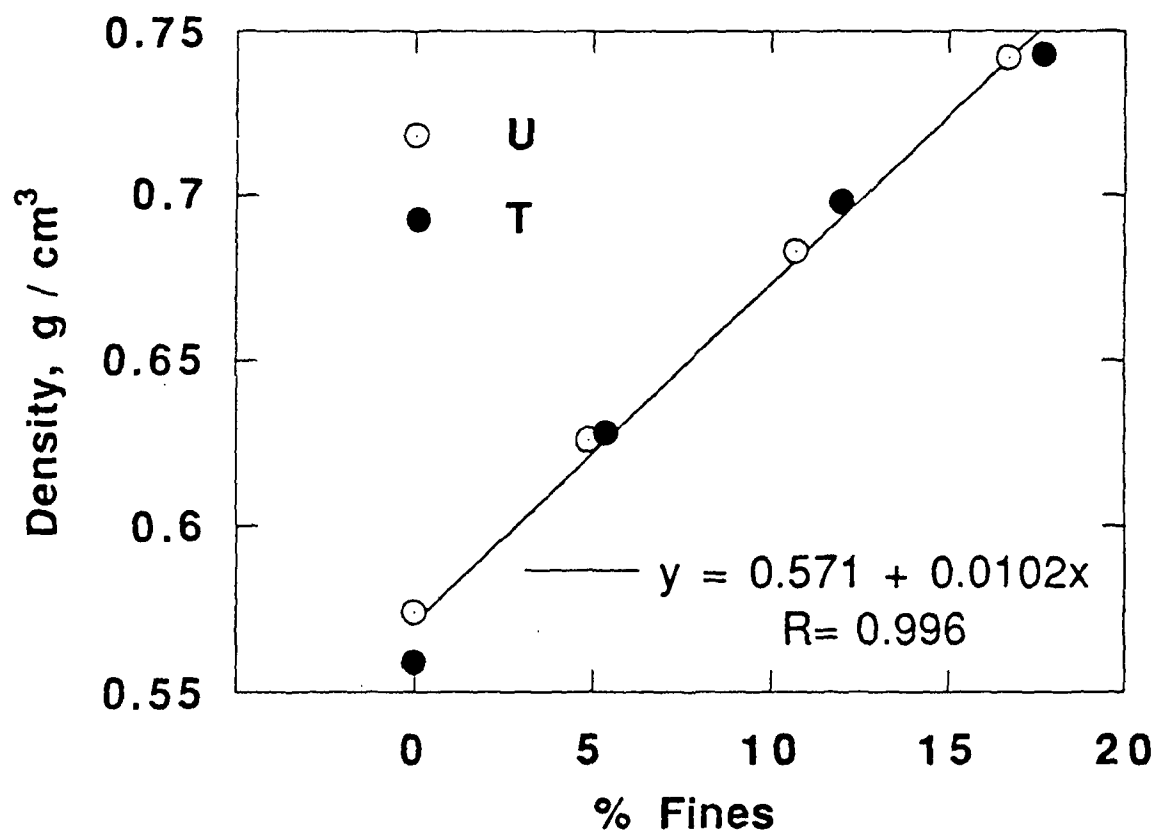


Fig. 10. Effect of strength aid treatment on the density of sheets as a function of percent fines in the sheet. Regression line shown includes the data for both treated (T) and untreated (U) sheets.

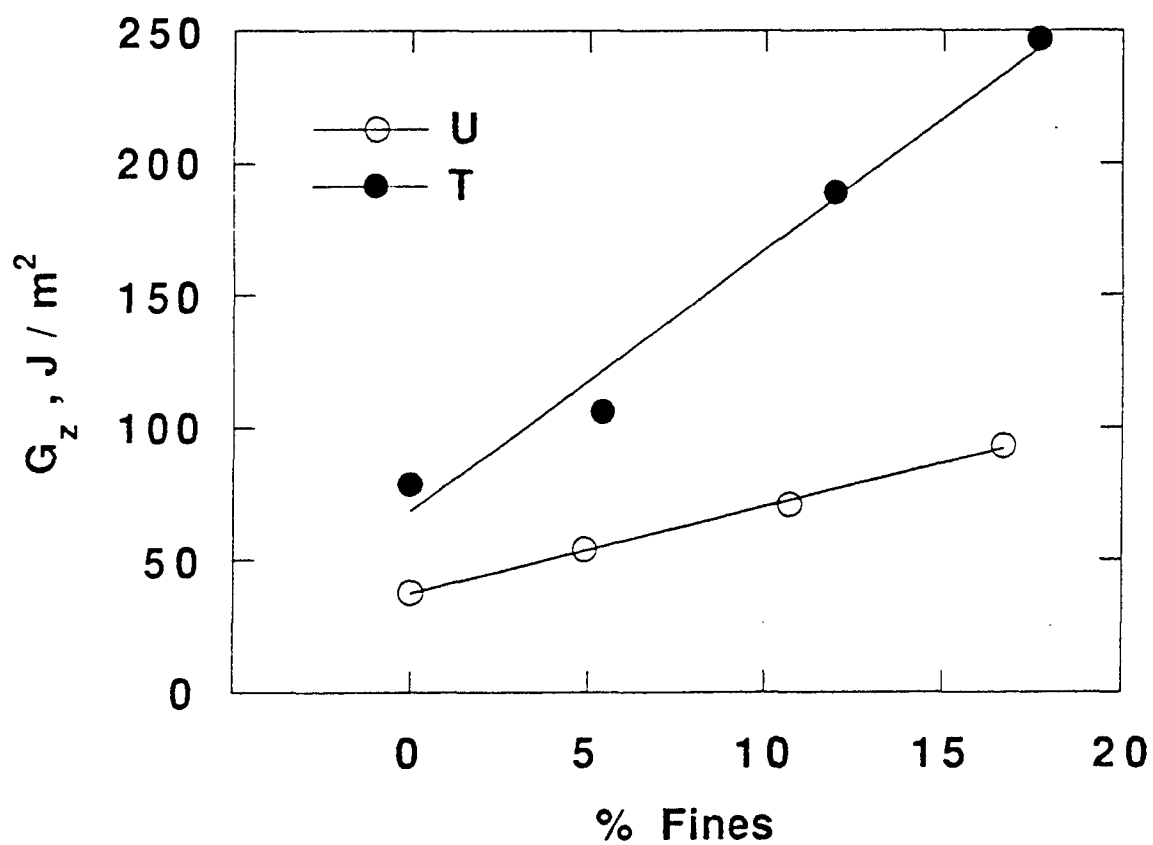


Fig. 11. Z-toughness as a function of percent fines in the sheet for treated (T) and untreated (U) sheets.

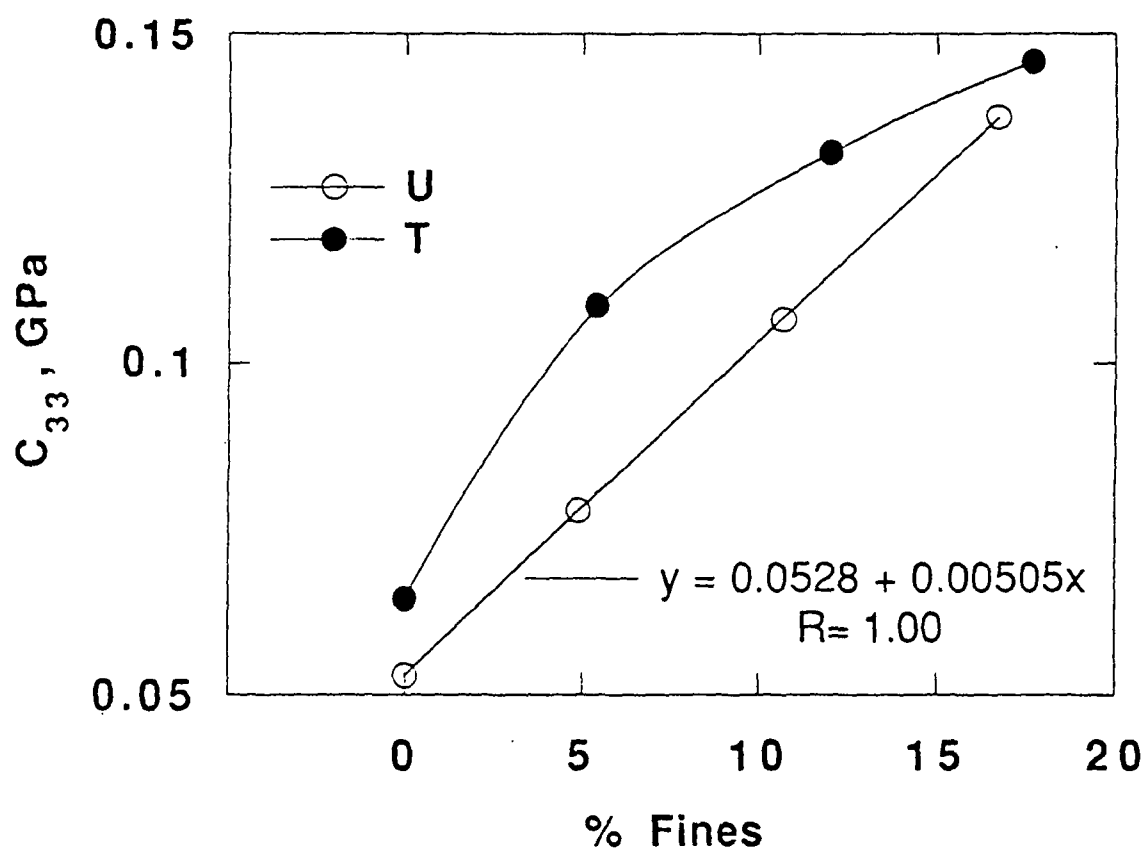


Fig. 12. Out-of-plane elastic stiffness as a function of percent fines in the sheet for treated (T) and untreated (U) sheets.

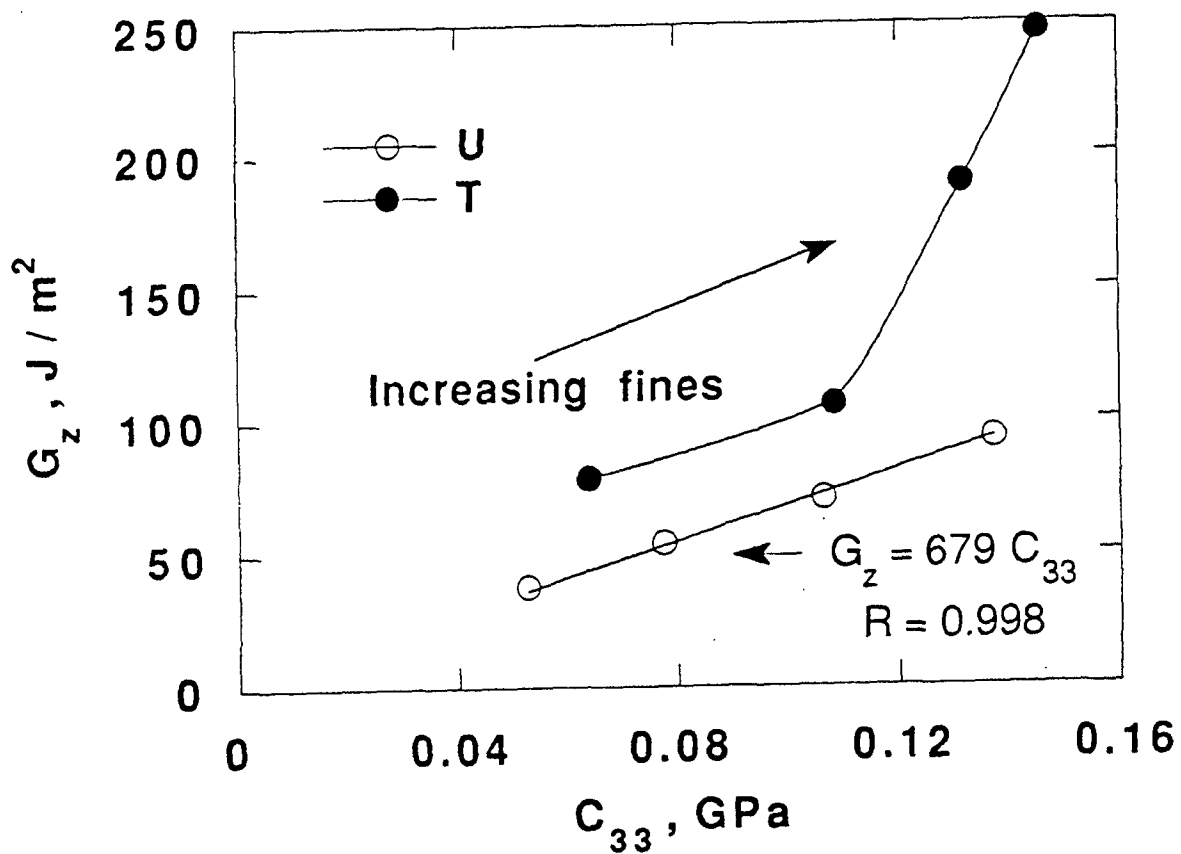


Fig. 13. Comparison of Z-toughness and out-of-plane elastic stiffness at increasing levels of fines for untreated (U) and treated (T) sheets.

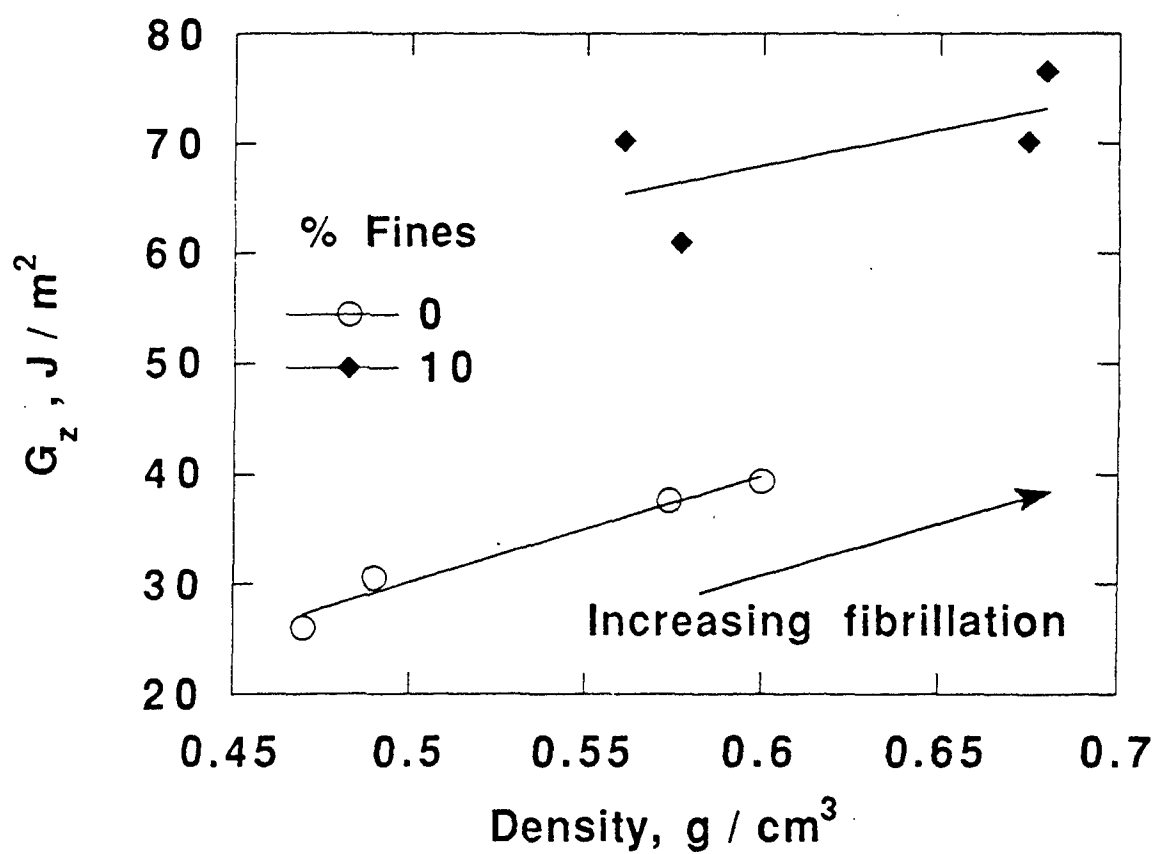


Fig. 15. Variation of Z-toughness with density at constant levels of fines and increasing fibrillation for untreated pulps.

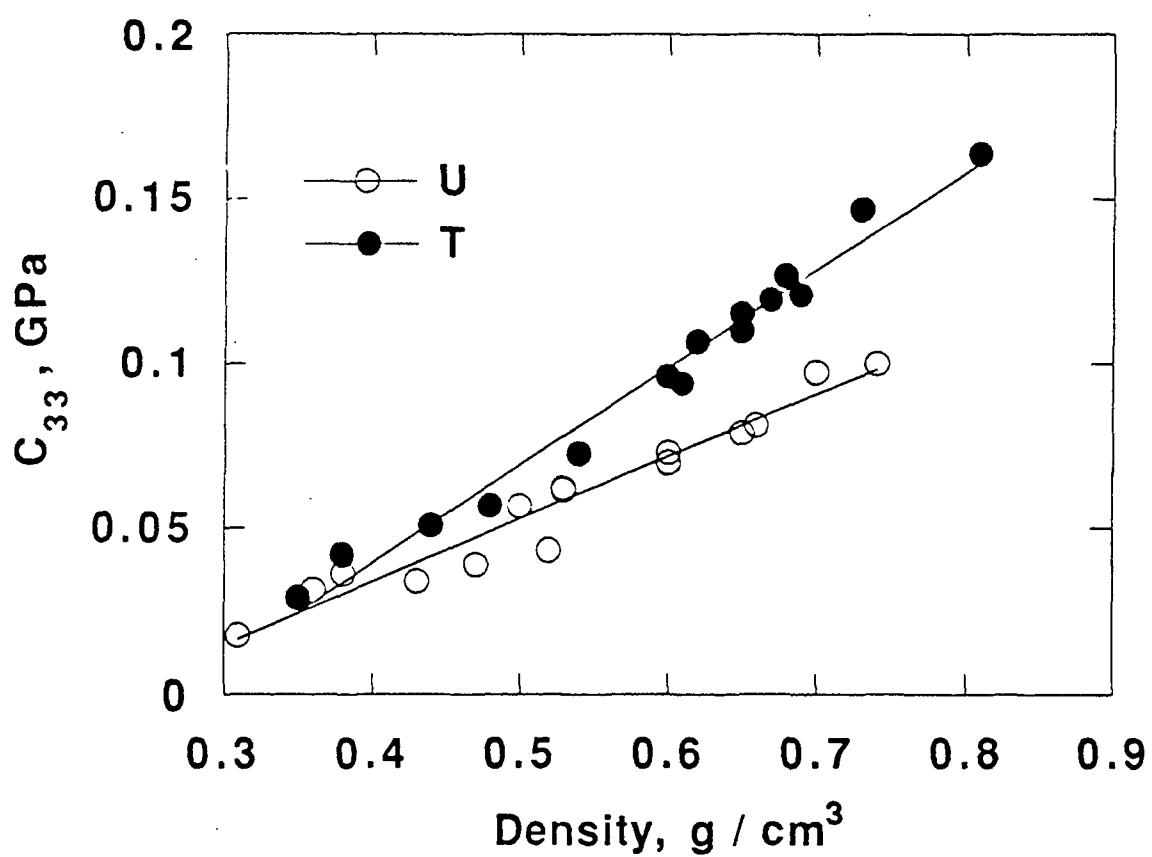


Fig. 16. Effect of strength aid treatment on the increase in out-of-plane elastic stiffness with density.

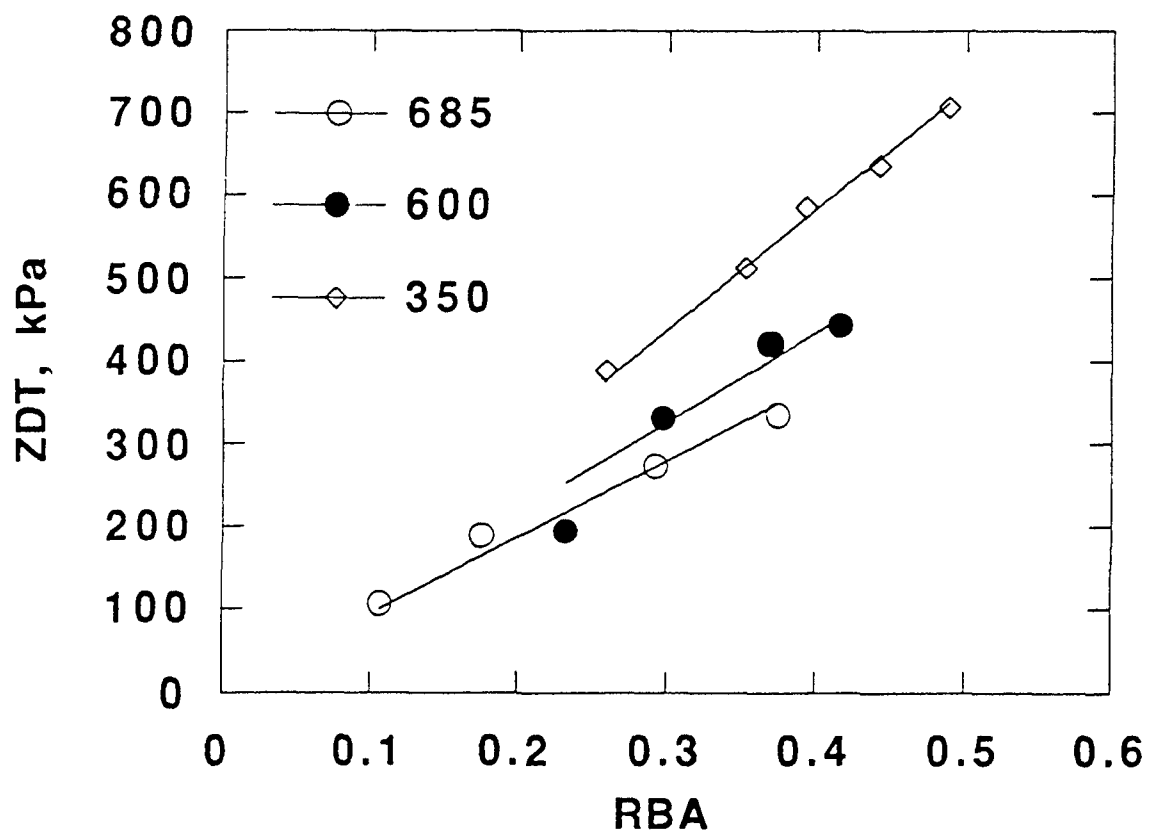


Fig. 17. Dependence of z-direction tensile strength on relative bonded area for whole, untreated pulps at the indicated freenesses. The linear regression lines are fit through the origin.

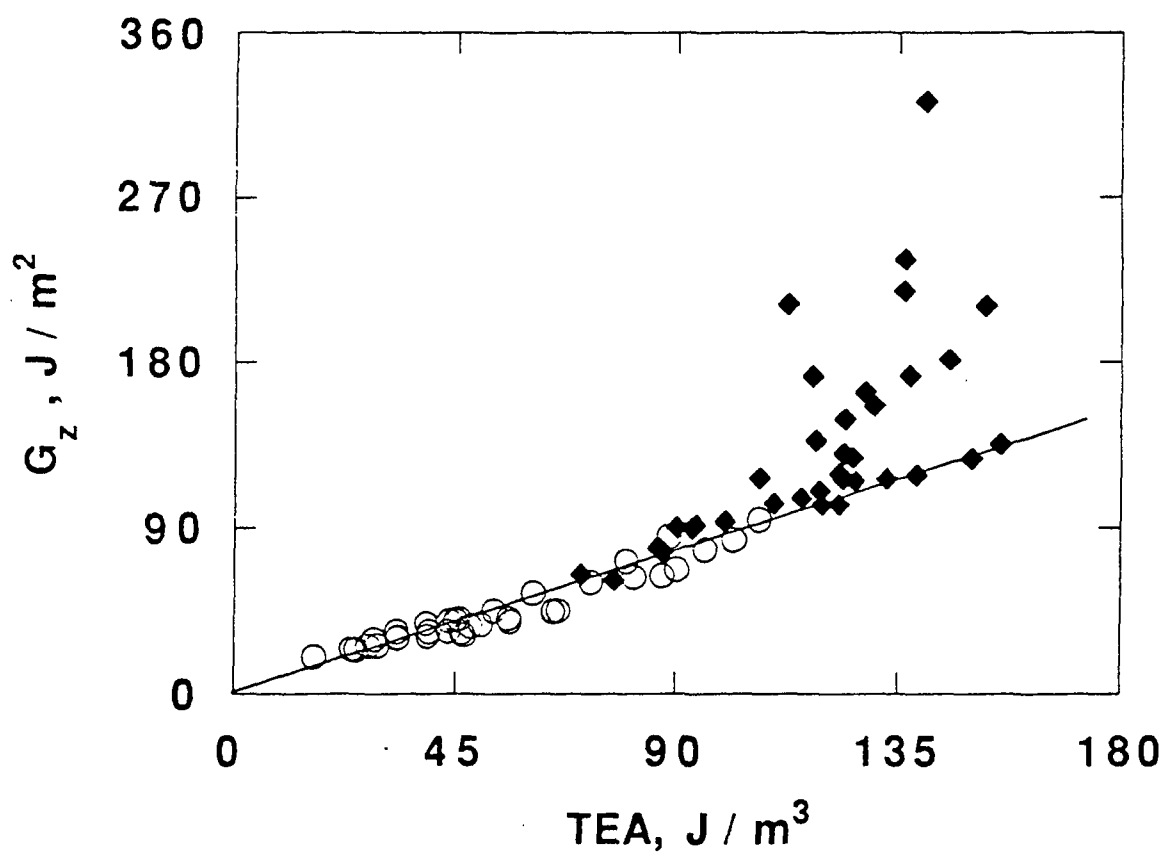


Fig. 19. Correlation of Z-toughness with tensile energy absorption for whole and classified, treated (filled symbols) and untreated (open symbols) pulps.

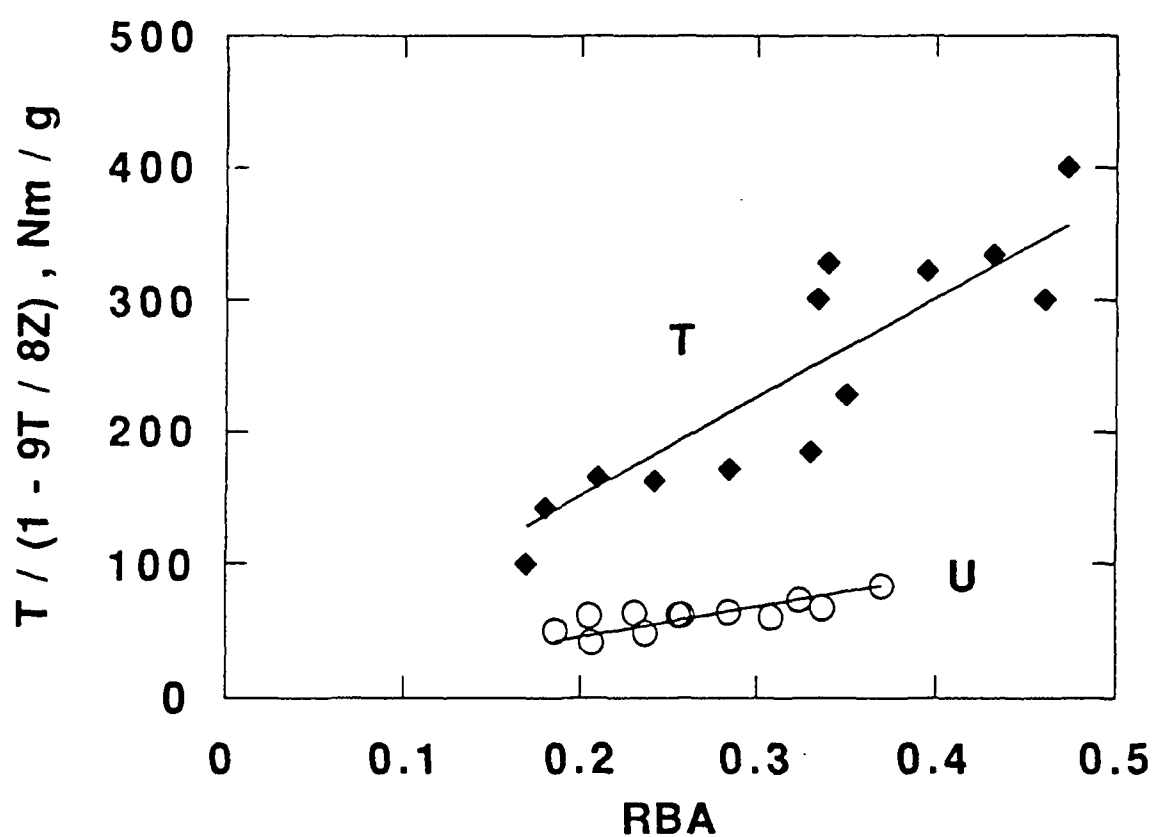


Fig. 20. Plot according to the Page equation for classified, untreated (U) and treated (T) pulps. Linear regression lines are fit through the origin.